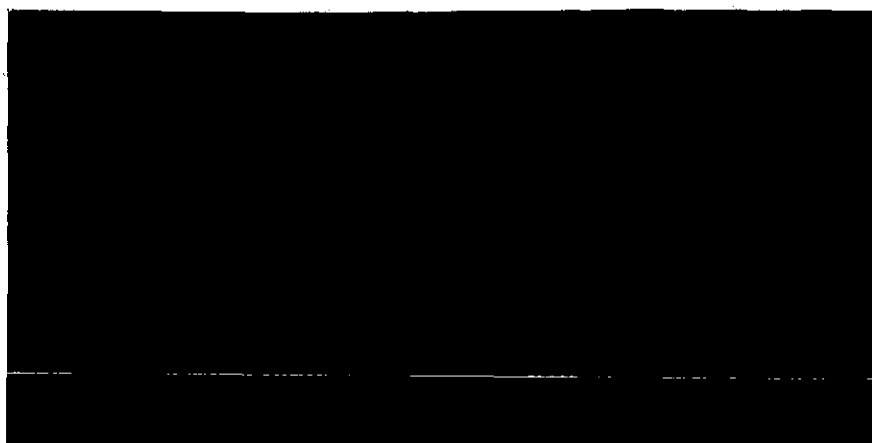

THE PERFORMANCE AND CAPABILITIES OF TERRESTRIAL ORGANISMS IN EXTREME AND UNUSUAL GASEOUS AND LIQUID ENVIRONMENTS



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MERCURY

Historical Review

It is impossible to say when man first discovered mercury, though the earliest evidence, a flask of metallic mercury found in a tomb at Kurna, Mesopotamia, indicates that he has been acquainted with the metal for at least 3,600 years. Other archeological investigations have determined that the ancient Egyptians made tin and copper amalgams of mercury. The Phoenicians and Carthaginians were acquainted with the metal before the Seventh Century B.C. (Egenhoff, 1953). Cinnabar, the most common mercury ore, appears to have been mined in such widely separated locations as Peru, China, Asia Minor and the Cyclades at least 2,000 years ago.

The first written records of the metal are those of Aristotle (320 B.C.) and Theophrastus in his *History of Stones* (ca. 300 B.C.). Aristotle's commentary discusses the metal as containing "much air and water" and mentions its use by priests (Egenhoff, 1953). Chinese commentaries on mercury date from around 200 B.C.

During the First Century A.D., Dioscorides, a Greek physician with Nero's army, mentioned the value of cinnabar as an eye medicine and for "heal[ing] burnings and the breaking out of pustules." Dioscorides also described the poisonous effects of mercury, suggesting milk or gold as remedies for the possible effects of ingested mercury. Hippocrates, too, recognized mercurial medicines.

Pliny the Younger's commentaries mentioned mercury's value in extracting gold, a practice that was to continue until the present time. Pliny's technique involved filtering a mercury-gold amalgam through a "well-tawed hide." The gold, he said, was left on the hide while the mercury trickles through.

The element took the name mercury sometime between the Sixth and Seventh Centuries A.D. when it was assigned the symbol of the planet Hermes (Mercury) which had previously been assigned to tin (Berthelot, 1889, quoted in Egenhoff, 1953). The association of the changeable metal with the fleet messenger, Mercury, is obvious.

Mercury fascinated the medieval alchemists who felt that the metal or its ore were necessary for the preparation of the philosophers' egg or stone, a compound which, it was believed, could transmute base metals to gold. The alchemists of the Middle Ages considered that all metals were some mixture of mercury and sulfur in varying degrees of imperfection. Ali Ibn Aina (Avicenna) offered the following observations in support of this conclusion:

...mercury, or something resembling it, is the essential constituent element of all the fusible bodies, for all of them are converted into mercury on fusion. Most of them, however, fuse only at a very high temperature so that their mercury appears red. In the case of lead, an onlooker does not doubt that this is mercury, since it melts at a lower temperature, but if during the fusion it is heated to the high temperature...its color becomes the same as other fusible bodies, i.e., fiery red. (Quoted in Egenhoff, 1953)

The sought after "stone" was assumed to be capable of supplying or removing the necessary proportions of sulfur and mercury from all metals so that they might be brought to perfection, i.e., converted to gold. Cinnabar was believed necessary in the synthesis of the philosophers' stone because it was thought to contain elements of baseness (sulfur) and perfection (silver). Mercury was commonly referred to as *argentum vivum* or "living silver." Avicenna considered mercury itself to be a compound, writing:

Mercury seems to be water with which a very tenuous and sulphurous earth has become so intimately mixed that no surface can be separated from it without something of that dryness covering it. (Quoted in Egenhoff, 1953)

During the medieval period calomel (HgCl) was prescribed as a cathartic. By the Sixteenth Century mercury was prescribed for several diseases. The mercury treatment for syphilis survives today in areas where penicillin is unknown or unavailable. Mercury compounds were also used as abortants and the chloride (HgCl_2) was a favorite poison for suicides. At this time two commentaries on mercury were published. Paracelsus (1533) produced a detailed description of mercury poisoning. Vanoccio Biringuccio (1540), a mathematician and metallurgist, published a commentary on mercury mining in which he accurately described the worst of mercury's toxic effects, damage to the nervous system:

[Mercury] has the property of contracting the nerves of those workers who extract it from the mine, if they

are not extremely careful; and those who handle it a long time find their limbs become weak and paralyzed.

De la Pirotechnia (1540) quoted in Egenhoff (1953).

Goldwater (1971) reports that in 1700 the citizens of Finale, Italy, brought suit against a local chemical plant that was manufacturing the corrosive sublimate (HgCl_2) of mercury and killing people with its smoke discharges. Napoleon, Ivan the Terrible and Charles II of England may have died of mercury poisoning (Goldwater, 1971). Charles II was known to have experimented with the metal in his own laboratory.

Research in the Twentieth Century

Abundance

Mercury is a relatively rare element. Of the naturally occurring elements, only 15 are less abundant. The abundance of mercury in the earth's crust has been estimated as between 30 and 60 ppb (Goldwater, 1971; Green, 1959, in McCarthy *et al.*, 1970). The metal is usually extracted from cinnabar, the native sulfide. Present world annual production is now about 10,000 tons (Goldwater, 1971) with the United States consuming nearly a third of this total. Spain, China, Mexico, the United States and the U.S.S.R. produce nearly all of the total.

Toxicity

Mercury produces two toxic syndromes in man depending on the form in which it is introduced. The first of these syndromes is produced by the inhalation of elemental mercury or the dusts of various inorganic compounds. Some inorganic mercury compounds may be taken up through the skin and the gastrointestinal tract. Relatively large amounts of metallic mercury may be ingested without harm. Acute inorganic mercury poisoning can produce nausea, vomiting and abdominal pain, and bloody diarrhea. Skin and mucous membranes show corrosive effects. Death may follow within ten days (Above from Merck Index, 1968). The chronic inorganic syndrome may produce an inflammation of the mouth and gums, excessive salivation, loosened teeth, kidney damage and a variety of neuromuscular disorders and personality changes. Magos (1967) has shown the brain-seeking properties of elemental mercury vapor.

The second major toxic syndrome of mercury is produced by organic mercury compounds. Phenyl mercurials are about as toxic as inorganic mercury compounds, but alkyl mercurials are much more toxic than any of the inorganic mercury poisons. These compounds are readily absorbed through the skin, causing a burning sensation that may be delayed for hours following exposure (Merck Index, 1968). The brain-seeking nature of alkyl mercurials may produce a complex of symptoms which resembles certain infections of the central nervous system.

For this reason, a diagnosis of alkyl mercury poisoning is often delayed (Study Group on Minimata Disease, 1966; Curley *et al.*, 1971). The symptoms of methyl mercury poisoning — the most common alkyl mercury poison — include neurasthenia, paresthesia, ataxia, narrowing of the visual field, hearing difficulties, emotional instability and a progressive loss of muscular control (Eyl, Wilcox and Reizen, 1970; Maximum Allowable Concentrations Committee, 1969).

It has been suggested that mercury may be an essential trace element because it is ubiquitous in living matter (Goldwater in P. and K. Montague, 1971). The fact that low levels of mercury exercise an inhibiting effect on a variety of enzymes tends to dispute this. Some of these effects are summarized in Table 1.

Minimata Disease and Organic Mercury Poisoning

The present concern for the hazards of organic mercury poisoning has its origin in the Japanese fishing village of Minimata. Between 1953 and 1965, 111 residents of Minimata were diagnosed as victims of organic mercury poisoning. Forty of these sufferers died (Study Group on Minimata Disease, 1966). Epidemiological studies showed that all of the afflicted group had eaten fish and shellfish from Minimata Bay. Examination of fish and shellfish from the bay verified that they contained significant amounts of methylmercuric chloride (CH_3HgCl). A plastics plant which dumped mercury wastes into the

Table 1. Examples of Common Enzymes Inhibited by Mercury Compounds.

Enzyme	Source	Reference
1 D amino acid oxidase	pig — kidney	Frishell 1957
2 amylase	black locust tree bark	Ewart 1953
3 ATPase	rat — kidney	Goth 1950
4 carbohydrases	pig — intestine	Larner 1956
5 catalase	beef — liver	Soher 1952
6 cellulase	<i>Myrothecium</i> (fungus)	Husain 1958
7 dehydrogenase (alcohol)	Yeast	Heitz 1968
8 diaphorase	<i>Myrothecium</i> (fungus)	Hilton 1955
9 glucose oxidation system	rat — brain, kidney	Cremer 1961
10 β -glucuronidase	<i>E. coli</i>	Doyle 1955
11 glutaminase	dog — kidney	Sayre 1958
12 glycogen phosphorylase system	crab — muscle	Sagardia 1969
13 homogentisic acid	rat — liver	Crandall 1955
14 hydrogenase	<i>E. coli</i>	Joklik 1950
15 Invertase	Yeast	Myrback 1957
16 Lipase	wheat germ	Singer 1948
17 malic dehydrogenase	<i>Myrothecium</i> (fungus)	Hilton 1955
18 malic oxidative decarboxylase	pigeon — liver	Rutter 1958
19 porphobilinogen deaminase	Spinach leaf	Bogorad 1957
20 phosphoglucose isomerase	rabbit — skeletal muscle	Chatterjee 1967
21 tyrosinase	<i>Agaricus</i> (fungus)	Owens 1953
22 urease	Jack bean	Evert 1952

bay was suspected as being the source, but all the polluting mercury was inorganic. Later, investigators found that the plant was in fact discharging some methyl mercury which had been produced as a byproduct of the mercury catalyzed conversion of acetylene to acetaldehyde. The amount was small — less than one percent of the total mercury discharged — but believed sufficient to explain the epidemic. In 1965 a similar incident occurred in Niigata, Japan.

Organic mercury compounds are used as fungicidal seed-dressings. Accidental ingestion of this seed has resulted in several tragedies (Eyl, 1971). The most frequent correlate of food poisoning from treated seed is poverty: In times of food shortage treated cereal seeds may be ground into flour with disastrous results. Ul Haq (1963) has reported the signs and symptoms of 36 patients suffering from mercury poisoning from poisoned flour. The Huckleby incident, a case involving an entire family in New Mexico which was afflicted with organic mercury poisoning, also involved treated seed (Curley *et al.*, 1971). Here, the seed was fed to pigs and the members of the family were affected when they ate the meat.

Much of the pioneering work on the hazards of organic mercury has come from Sweden where organic mercurials have been in wide use as agricultural fungicides since the early 1940's (Lofroth and Duffy, 1969). In the early 1950's, Swedish conservationists observed unusual mortality in wild birds which had eaten the treated seed.

Subsequent studies showed amounts of mercury in food products which were significantly higher than those in foods from areas where there was no widespread use of organic mercury fungicides.

Biological Alkylation

High levels of methyl mercury were also found in some fish and birds which preyed on fish such as the eagle (Johnels *et al.*, 1968). Jensen and Jernelov (1969) conducted experiments with a model ecosystem containing fish, sediments and water. They found that added inorganic mercury was ultimately concentrated in the fish's tissues as methyl (HgCH_3^+) mercury and that the site of conversion was in the sediment. Johnels and Olsson (cited in P. and K. Montague, 1971) predicted that inorganic mercury might be converted to methyl mercury by microorganisms in anaerobic sediments. Such a biological alkylation had earlier been suggested as a possible explanation for the Minimata tragedy (Kurland, 1960, cited in Dunlap, 1971; Fujiki, 1963, cited in Wood, Kennedy and Rosen, 1968). This capability of microorganisms had already been recognized with arsenic and selenium (Challenger, 1955).

As a result of Jensen and Jernelov's discovery, several mechanisms for the biological methylation of mercury have been proposed. Wood, Kennedy and Rosen (1968; Dunlap, 1971) believe that vitamin B₁₂-containing enzyme systems should be capable of methyl mercury synthesis. Their scheme is based on the observation of Halpern and Maher (1964,

cited in Wood, Kennedy and Rosen, 1968) that methylpentacyanocobaltate reacts with the Hg^{++} ion to produce methyl mercury. Methylcorrinoid derivatives are the only major coenzymes capable of transferring methyl groups as carbanions (CH_3^-), carbonium ions (CH_3^+) or the radical ($\text{CH}_3\cdot$). Proceeding from this assumption, Wood has developed schemes involving methionine synthetase, acetate synthetase and methane synthetase which could produce methyl mercury. All of these enzyme systems are known to exist in anaerobic organisms. Wood has demonstrated the synthesis of mono- and dimethyl mercury by methylcobalamin in both enzymatic and non-enzymatic systems.

Landner (1971) conducted methylation studies with *Neurospora crassa* and proposed that the biological methylation of mercury amounts to an incorrect methionine synthesis. In his scheme, mercury is complexed to homo-cysteine and the methyl group is transferred to this complex. Presumably, the methyl mercury-homocysteine complex can no longer exercise feedback control over the methylating enzymes and the reaction will proceed until homocysteine becomes limiting. Methionine will suppress the methylation when it is added to the liquid culture medium.

The initial reports of mercury in fish concerned freshwater fish. Westermarck and Johnels (1964 cited in Aberg *et al.*, 1969) reported elevated mercury levels in fish exposed to mercury wastes from chloralkali and paper pulp plants. Noren and Westo8 (1967, cited in Aberg *et al.*, 1969) identified the mercury in freshwater

fish as nonmethyl derivatives. Rosen (1969, cited in Aberg *et al.*, 1969) has stated that regardless of its form when introduced to the environment, mercury can and will be methylated.

The Mercury in Fish Scare

In early 1970, Norvald Fimreite of the University of Western Ontario released a report which showed high levels of mercury in freshwater fish taken from Lake Saint Clair, a body of water connecting lakes Huron and Erie (P. and K. Montague, 1971). The source of this mercury was apparently a chloralkali plant and a chemical plant which discharged wastes into waterways feeding the lake. This report was followed by several others from different parts of the United States and Canada which also showed fish with mercury contents exceeding the United States Food and Drug Administration's rejection standard of 0.5 ppm fresh weight. Many states banned fishing on bodies of water suspected of being polluted. Other posted guidelines for the consumption of potentially tainted fish. Pregnant women were frequently advised to avoid suspected fish altogether because it was known that the fetus can be even more susceptible to organic mercury poisoning than the mother (Eyl, 1970).

This phase of mercury research is hard to document at the present because so many reports of mercury contaminated fish are being released through press conferences rather than the usual journals

for scientific communication. This is understandable because a matter of public health is involved. Public health agencies are charged with investigating the mercury content of fish and they are under pressure from several groups to release their findings as soon as possible. Since there is only one standard of rejection for food products in the United States, the FDA's 0.5 ppm limit, these agencies must issue warnings on all fish products exceeding this amount. Therefore, one can read that fish in such-and-such a part of the country were found to be "contaminated" and ordered off the market or not to be consumed, but there are none of the details which would regularly be given in a scientific journal and therefore no way of evaluating sources of error.

Method is very important in mercury research. It is only recently that researchers have had a relatively inexpensive technique for low level determination of mercury. This technique is flameless atomic absorption (Hatch and Ott, 1968). The method is quite sensitive; 0.01 micrograms of mercury can readily be detected, but "precision and accuracy are only moderate" (Study Group on Mercury Hazards, 1971). In the hands of an unskilled operator this technique offers plentiful sources of error. This is an important observation because flameless atomic absorption is the preferred technique in nearly all state and federal health laboratories and commercial analysis firms. In these institutions the operator is often just doing a job: The precision necessary for some kinds of research may

be of no concern. There have been two recent studies evaluating the precision of a sample of laboratories in low level metal determination which have revealed that errors of several hundred percent are common (Johanesen, 1971; Donovan, Vought and Rakow, 1971).

The most precise method of sub-microgram mercury determination is neutron-activation analysis. This method has a reported precision of ± 2 percent (Study Group on Hazards of Mercury, 1971), but is expensive and inaccessible to many researchers. A nuclear reactor is needed as a neutron source. Gas chromatography is also more precise than flameless atomic absorption and offers the advantage of showing the form in which the mercury is present. The technique is, however, more complicated and requires a well-trained operator.

Despite the errors inherent in these techniques, it seems likely that many of the reports of mercury contamination in freshwater fish are accurate. The Swedish work relies heavily on neutron activation and gas chromatographic analysis. Fimreite's work on Lake Saint Clair also used neutron activation analysis. In several of these investigations the emission sources were readily identified and the magnitude of their discharges were shown to be sufficient to account for the results. The reports of mercury in ocean-going fish are harder to evaluate.

In late 1970, Bruce McDuffie of the State University of New York at Binghamton reported that canned tuna obtained from a local

grocery store contained 0.75 ppm mercury on a fresh weight basis (P. and K. Montague, 1971). This was followed by an FDA ban on several lots of canned tuna suspected, because of spot checks, of exceeding the 0.5 ppm standard. In 1971 the FDA issued a warning on swordfish has been often attributed to a food chain effect; natural or pollutant mercury becomes concentrated with higher and higher trophic levels. Tuna and swordfish, because they are top carnivores, have the highest mercury content. The FDA laboratories have released data showing that the mercury content of these fish is proportional to their weight: The larger the fish, the greater the mercury content. Bache, Gutermann and Lisk (1971) have shown a similar relationship with a freshwater fish, the lake trout. Not only does the lake trout's mercury content increase with age, but the ratio of methyl mercury to total mercury in the body also increases.

Complicating the whole problem of mercury in fish is the observation that there are indications that fish may naturally accumulate the metal to higher levels than many other organisms (Stock and Cucuel, 1934). There have been no studies showing the mercury levels at various trophic levels in the tuna or billfish food chain. These are urgently needed.

Klein and Goldberg (1970) have calculated that mercury enters the seas at about equal rates from both continental weathering and industrial processes. Goldberg (1965 cited in Klein and Goldberg, 1970) estimates the time of residence for mercury in open seawater

as 10^4 years. This suggests that human activities have yet to contribute significant amounts of mercury to the general marine environment. There have been allusions in the popular press to a variety of studies showing that canned or preserved fish over fifty years old contain amounts of mercury which exceed the FDA's rejection standard. Miller *et al.* (1972) have reported that preserved tuna from both Atlantic and Pacific Oceans caught between 1878 and 1909 contain between 0.3 and 0.6 ppm mercury, comparable to contemporary values. Goldwater (1971) has attacked a recent report of methyl mercury poisoning in an habitual swordfish eater as erroneous because a "spontaneous remission" (as apparently claimed by the reporting physician) is highly unlikely in chronic methyl mercury poisoning.

It may well be that the mercury levels in ocean-going fishes are normal and yet still dangerous. The Swedish Committee on Evaluating the Toxicity of Mercury in Fish (1970 cited in Study Group on Hazards of Mercury, 1971) has set the allowable daily intake of mercury (as the alkyl) at 0.03 milligrams. This figure was arrived at by taking the lowest value of mercury in whole blood reported in persons showing toxic symptoms, 0.2 μg . per gram, and dividing by a safety factor of 10. Based on research on the retention of ingested mercury compounds, this safe level of 0.02 μg . per gram blood will be achieved by the weekly consumption of 210 grams (about seven ounces) of fish containing 1.0 ppm mercury as methyl mercury.

Mercury in the Environment

Rankama and Sahama (1950) report that marine algae contain "more than a hundred times" as much mercury as is present in a comparable volume of seawater. Seawater appears to contain between 0.01 and 0.03 μg . mercury per liter. A recent review of mercury in the environment (USGS, 1970) says that this concentration factor in marine phytoplankton may range between 250 and 3,000 times and be as high as 100,000 times in "other forms of sea life." Klein and Goldberg (1970) found a variety of marine animals which had concentrated mercury to levels 500 or more times that of the ambient water. Glooschenko (1969) found that the marine diatom *Chaetoceros costatum* concentrated mercury by a passive uptake at its surface. Burton and Leatherland (1971) found that the mollusk *Mercenaria mercenaria* taken from waters containing about 0.01 ppb mercury itself contained 0.18 to 0.57 ppm. The mud below the mollusk contained 0.19 to 0.64 ppm mercury at its surface and 2.2 to 5.7 ppm in the anaerobic layers at a depth of 10 cm. Harris, White and MacFarlane (1970) found that several of the popular organomercury fungicides could inhibit photosynthesis at levels as low as 0.1 ppb.

While marine phytoplankton appear to concentrate the mercury in their environment, the effect is slight in terrestrial plants (Schacklette, 1970). Most plants contain less than 0.5 ppm mercury in their dry matter. The average soil in the United States contains

about 0.1 ppm mercury in its dry matter. Soils overlying mercury deposits may contain as much as 40 ppm mercury. Plants from these soils average about 3.5 ppm mercury in their dry matter. That plants can be a substantial reservoir of mercury is seen in the fact that coal, a plant product is a significant source of environmental mercury (Anon., 1970; Joensuu, 1971). Yeaple (1972) reported mercury levels up to 2.0 ppm in moss samples from various New England sites. Mercury levels in the mosses were generally higher in urban areas. There have been reports that plants can concentrate mercury as the metal. Rankama and Sahama (1950) reported the presence of drops of metallic mercury in the seed capsules of the chickweed *Holosteum umbellatum*. Goldschmidt (1954 cited in Shacklette, 1970) says that metallic mercury occurs under a moss forest cover in the vicinity of an hydrothermal mercury deposit in the Rhine Palatinate. Schacklette (1970) found no evidence of this phenomenon in an examination of the flora in the vicinity of a mercury smelter.

Sources of Mercury in the Environment

Mercury is unique among the metals in having an appreciable vapor pressure at room temperature. Several of the naturally occurring inorganic compounds of mercury including the common ore, cinnabar (HgS), have low boiling points (Table 2). The element has two valence states, Hg_2^{++} and Hg^{++} , and a dynamic and complex coordination chemistry.

Table 2. Boiling Points of Selected Mercury Compounds.

Compound	Boiling, sublimation (S) or decomposition (D) point
Hg	356.58
Hg ₂ Br ₂	S 345
HgBr ₂	322
Hg ₂ Cl ₂	S 400
HgCl ₂	302
Hg ₂ I ₂	S 140, D 290
HgI ₂ (β-form)	354
Hg ₂ O	D 100
HgO	D 500
HgS	S 583.5

Air above mercury deposits may contain as much as $20 \mu\text{g./M}^3$ (USGS, 1970). This value drops off rapidly, decreasing by several hundred times at an altitude of 130 meters. The mercury content of the air above these deposits has a distinct daily cycle, reaching a maximum at noon and a minimum in the early morning. A similar cycle has been predicted for the lunar day (Reed, Goleb, Jovanovic, 1971). Lunar rock samples contain mercury which is easily volatilized at lunar daytime temperatures (*ca.* 120°C.).

Vulcanism is apparently a significant source of atmospheric mercury (White, Hinkle, Barnes, 1970; Eshleman, Siegel, Siegel, 1971). The condensate from fumaroles in the Kuriles was measured as between 0.3 and 6.0 ppb mercury. Fumarole gases in the same study contained as much as $4 \mu\text{g./M}^3$. Fumaroles of Hawaiian volcanoes can produce over $20 \mu\text{g./M}^3$ (Eshleman, Siegel, Siegel, 1971). Volcanic muds from Yellowstone, Wyoming contain as much as 150 ppm mercury while sediments from the same area have as much as 500 ppm. Precipitates from hot springs at Sulfur Bank, California, have yielded 5000 tons of metallic mercury to mining operations (USGS, 1970).

Rain contains 0.2 ppb mercury on the average (USGS, 1970). Fresh stream and river water usually contains less than 0.1 ppb, though as much as 25 times this amount may be held in suspended particulates (Jenne, 1970). In 1970 the United States Geological Survey conducted a survey of river and stream water in 31 states. Sixty five percent

of these waters had less than 0.1 ppb soluble mercury (USGS, 1970); fifteen percent contained more than 1.0 ppb, while three percent exceeded 5 ppb, the Food and Drug Administration's rejection standard for drinking waters. Sediments underlying these waters averaged 200 ppb.

Background levels of atmospheric mercury appear to be between 1.0 and 10.0 nanograms per cubic meter (USGS, 1970). Background levels are lower over oceans than over land and highest in urban areas, reflecting the contribution of industrial sources. The largest source of industrial mercury air pollution is the combustion of fossil fuels. Bituminous coals may contain 1-25 ppb Hg. Anthracites can contain as much as 2,700 ppb. Crude petroleum contains as much as 21,000 ppb, while tarry fractions which have lost the more volatile hydrocarbons may contain as much as 500,000 ppb.

The 1969 United States industrial consumption of mercury is summarized in Table 3. Chloralkali production, the separation of NaOH and chlorine from seawater by the electrolysis of brine, is the biggest industrial use of mercury. Here, mercury is used as a flowing cathode. Losses of mercury from the chloralkali process can be significant sources of environmental pollution both through losses from the plant itself and contamination of the products (Siegel and Eshleman, 1971 unpublished).

During the 1849 California Gold Rush large quantities of mercury were used to prepare gold amalgams. Pure gold was then separated

Table 3. Industrial Consumption of Mercury.

	1969 consumption ^a
Chlor-alkali production	1575
Electrical apparatus	1417
Paints	739
Industrial and control instruments	531
Dental preparations	232
Catalysts	225
Agriculture ^b	204
General laboratory use	155
Pharmaceuticals	55
Pulp- and papermaking	42
Other uses ^c	736
Total	5911

^a Thousands of pounds.

^b Includes fungicides and bactericides for industrial purposes.

^c Includes university and other research, and government allocation for military and scientific purposes.

Source: U. S. Bureau of Mines.

by boiling off the mercury — with fatal results to not a few miners — at relatively low temperatures. It has been estimated that over one million flasks of mercury (a flask is the unit of commerce: 76 pounds) or 76,000,000 pounds were consumed in California during the years following the discovery of gold. None of this mercury has been recovered.

The extent of man's contribution to the overall amounts of mercury in the environment is unclear. Certainly man has been shown to be a mercury polluter on several occasions, but his role in spreading this metal is probably not as great as that in broadcasting lead throughout the environment.

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MERCURY CONTAMINATION IN HAWAII

Before 1970, there were no reports of the presence of mercury in the Hawaiian environment. Late in that year, local newspapers carried reports of high levels of mercury in the sediments of Keehi Lagoon in Honolulu. Coming as they did, at a time of increasing worldwide awareness of the hazards of environmental mercury contamination, these accounts inspired the concern of both the public and the scientific community. From this concern came the first survey of mercury in Hawaii (Siegel *et al.* 1971). Subsequent studies have tried to identify the sources and modes of dispersal of the element, matters of special interest in an island system which is lacking in the commonly recognized industrial sources of mercury contamination. This paper will attempt to summarize the available data on mercury in the Hawaiian environment and assess the relative importance of natural and industrial sources.

Materials and Methods

(a) Atomic Absorption

All mercury analyses involved variations of the flameless atomic absorption technique (Hatch and Ott 1968) wherein samples are oxidized so that any mercury present is in the form of the mercuric (Hg^{++}) ion. Stannous ion is then added to the sample with the result that

mercury is reduced to the metal (Hg^0) according to the reaction $\text{Hg}^{++} + \text{Sn}^{++} \longrightarrow \text{Hg}^0 + \text{Sn}^{++++}$. The gaseous metallic mercury thus liberated is swept from the reaction vessel by a carrier gas (usually dry, filtered air) into an absorption cell. The quantity of mercury present is read as the optical density of the gas in the cell at the 2533.65 Å mercury resonance line. The method is quite sensitive having a reliable limit of detection (O.D.=0.0044) of 0.01 micrograms (μg) of mercury and is relatively free from interferences.

Most analyses were performed with a Utopia Instruments mercury analysis kit (Mittelhauser 1970) with a 10 cm absorption cell mounted in the light path of a Beckman 1301 atomic absorption system and Beckman DB-G spectrophotometer. This is an open system: All mercury evolved is exhausted after passing through the absorption cell. Later analyses were performed with a Coleman MAS-50 mercury analyzer, a self-contained atomic absorption unit which recirculates the mercury evolved allowing longer observation of peak O.D. values. Cross checks of these instruments with similar analytic systems in other laboratories have failed to reveal any machine errors.

(B) Standards

A mercury stock solution was prepared by dissolving 0.1354 g of reagent grade HgCl_2 in 100 ml of deionized water ($1000 \mu\text{g ml}^{-1}$). A working standard solution of $1.0 \mu\text{g ml}^{-1}$ was prepared daily by dilution from the stock solution. For most analyses, a series of

standards containing 0.0, 0.05, 0.10, 0.20, 0.50, and 1.00 $\mu\text{g Hg}$ are sufficient for preparation of a calibration curve.

(C) Sample Collection and Preparation

Biological materials were wet-ashed in either a 2:1 solution of HNO_3 (70% reagent) and H_2O_2 (30% reagent) or a 2:1 solution of HNO_3 and HClO_4 (70% reagent). The nitric-perchloric mixture is most efficient at breaking down resistant plant cell wall materials. Soils, sediments and rocks were digested in various solutions including $\text{HNO}_3:\text{HClO}_4$, $\text{HNO}_3:\text{H}_2\text{O}_2$, aqua regia, and HF. Water samples were acidified with a few drops of HNO_3 at the time of collection, filtered and analyzed directly. Field air samples of 0.2-0.4 m^3 were collected with a portable battery operated pump (Mine Safety Appliances No. 92813, 92814). Air was drawn through a trap containing either concentrated HNO_3 or $\text{H}_2\text{SO}_4:\text{HNO}_3$ (10:1) and 0.5 g powdered reagent grade copper.

Rainwater samples were obtained from a network of primary and secondary weather stations operated by the United States Weather Service. Each weather station was supplied with a 1.0 liter polyethylene bottle fitted with a 10.0 cm polyethylene funnel, both of which had been acid washed to remove any possible mercury contaminant. These rain traps were mounted beside the Weather Service's rain gauge at a height of at least 1.0 m to minimize possible splash effects. A trap filled with laboratory deionized water was retained as a blank.

At the end of a 7 day collection period, the rainwater in the traps was acidified with a few drops of HNO_3 and trap bottles were then sealed and returned to the laboratory in Honolulu for mercury analysis.

(D) Statistical Analysis

The regression line for the Ala Wai Canal data (Table 4, Fig. 5), were obtained using a program for an IBM 360 computer system prepared by the University of California at Los Angeles Health Science Computing Facility.

Results and Discussion

Joensuu (1971) has suggested that fossil fuels may be a potential source of mercury pollution. Weiss *et al.* (1971) analyzed the mercury levels in snow strata from Greenland Icecap and concluded that although natural processes contribute the larger portion of atmospheric mercury, human activities are responsible for increased dissemination of the element in recent decades. Dickson (1972) has attacked these conclusions, arguing for a greater human contribution to the worldwide distribution of the element.

To investigate the possible mercury release from fossil fuel combustion, the mercury contents of soils and vegetation samples from Ala Moana Park in urban Honolulu were analyzed. This site is adjacent to a major thoroughfare, Ala Moana Blvd., which carries

Table 4
Mercury^a in the Ala Wai Canal and Yacht Harbor

Site	July 7	July 14	March 6
Harbor Entrance	—	210 ^b	—
Texaco Dock ^c	210	460	1,340
Texaco Midchannel	300	440	690
Hawaii Yacht Club	—	—	730
Skindivers Hawaii	—	—	1,090
Ala Moana Bridge	280	520	570
KPOI	170	400	620
Kalakaua Bridge	240	440	310
McCully Bridge	140	410	290
Kuamoo Street	—	—	400
Manoa-Palolo Drainage Canal	40	140	230
Manoa-Palolo Canal Dock	—	70	—
Kanekapolei St.	—	—	350
Paokalani St.	—	—	90
Kapahulu Blvd.	110	120	—

^a Expressed as $\mu\text{g kg}^{-1}$ dry matter.

^b Expressed as $\mu\text{g kg}^{-1}$ fresh weight (dry weights unavailable, but water content of these sediments was probably ca. 50%).

^c Sediments samples at stated location; other site designations refer to midchannel samplings opposite the named landmark.

at least 60,000 automobiles per day and the parking facilities of the Ala Moana Shopping Center which can and frequently does accommodate over 7,000 cars. Plants and soils in the park have been shown to be heavily contaminated with lead and zinc which originated from gasoline and oil additives and tire casings. Figure 1 shows the mercury contents of park soils and vegetation along a transect line extending from the medial strip of Ala Moana Blvd. (0.0M) across the grass covered athletic field of the park to a smaller access road (137.0M). Included for reference are the data for lead along the same transect line (Fig. 2).

The results seem paradoxical. To be sure, there is a similar peak in the levels of the two metals in the surface soil of the shoulder of the smaller park road (137.0M), but the shapes of the lead and mercury lines are quite different along that portion of the transect extending from the medial strip of Ala Moana Blvd. to a point 10.0m south of the shoulder of the road. If one accepts the hypothesis that automobile exhausts are the source of both the lead and mercury along this transect, further explanation is needed.

The atomic masses of mercury (200) and lead (207) are close. Lead appears in automobile exhausts as a complex mixture consisting largely of oxides and halides. Mercury, if present, should form similar compounds. The molecular weights of these exhaust products being close should exclude fractional precipitation from the exhaust aerosol as an explanation for differing concentration gradients in

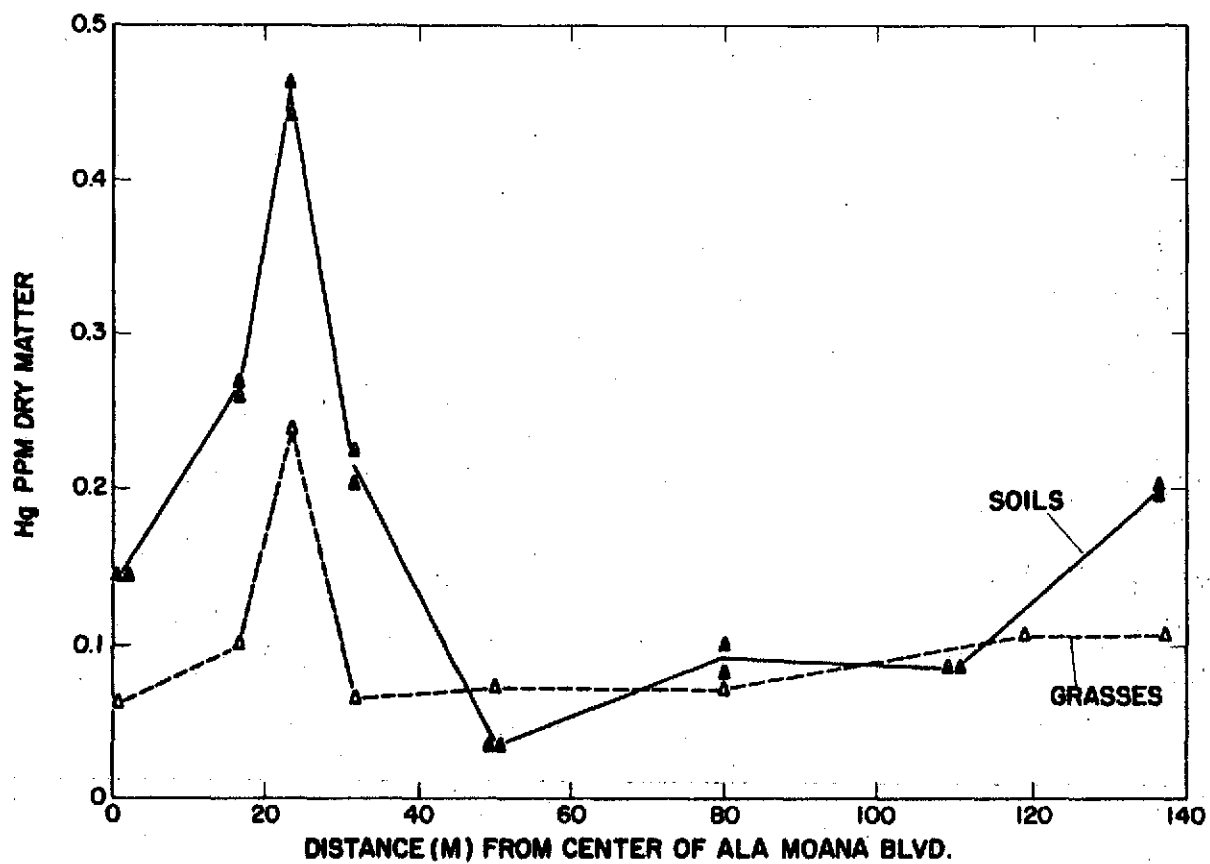


Fig. 1. Mercury in Ala Moana Park soils and grass.

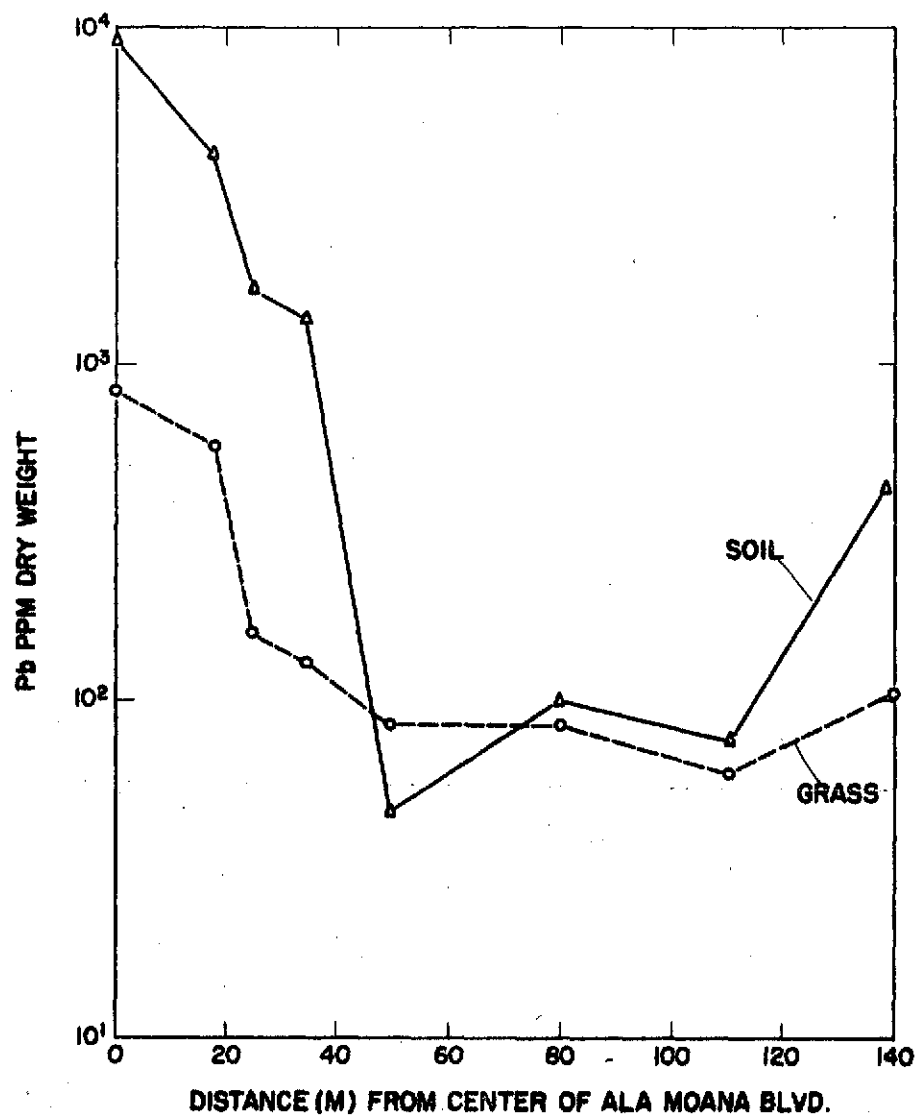


Fig. 2. Lead in Ala Moana Park soils and grass.

roadside plants and soils. Many mercury compounds have appreciable vapor pressures at relatively low temperatures. Figure 3 shows the temperature at the ground surface and 3 cm above ground along that portion of the transect closest to the roadway. The lowest values for mercury correspond to the highest air and soil temperatures suggesting that if the initial concentration of mercury in exhaust aerosol is greatest toward the center of the road, high surface temperatures and the prevailing NE trade winds may combine to keep the metal in suspension. Thus, a complex interaction of exhaust concentration, temperature and wind could cause the peak mercury fallout to be displaced some downwind of the roadway as observed. Data on the mercury contents of exhaust and gasoline is needed.

Less than 200 m. from the western boundary of Ala Moana Park lie the Ala Wai Canal and Yacht Harbor. The Canal was dug in 1927 to provide drainage for the Waikiki resort area of Honolulu. The canal communicates with the yacht harbor at the Ala Moana Bridge (Fig. 4) forming a continuous body of water extending over 2 kilometers in from the sea. In 1969 it was disclosed that the waters in the Canal contained concentrations of coliform bacteria which exceeded Hawaii State Department of Health standards (Cox 1969, Gonzalez 1971). In 1971 an analysis of the sediments in the Ala Wai was begun in an attempt to assess the degree of heavy metal contamination.

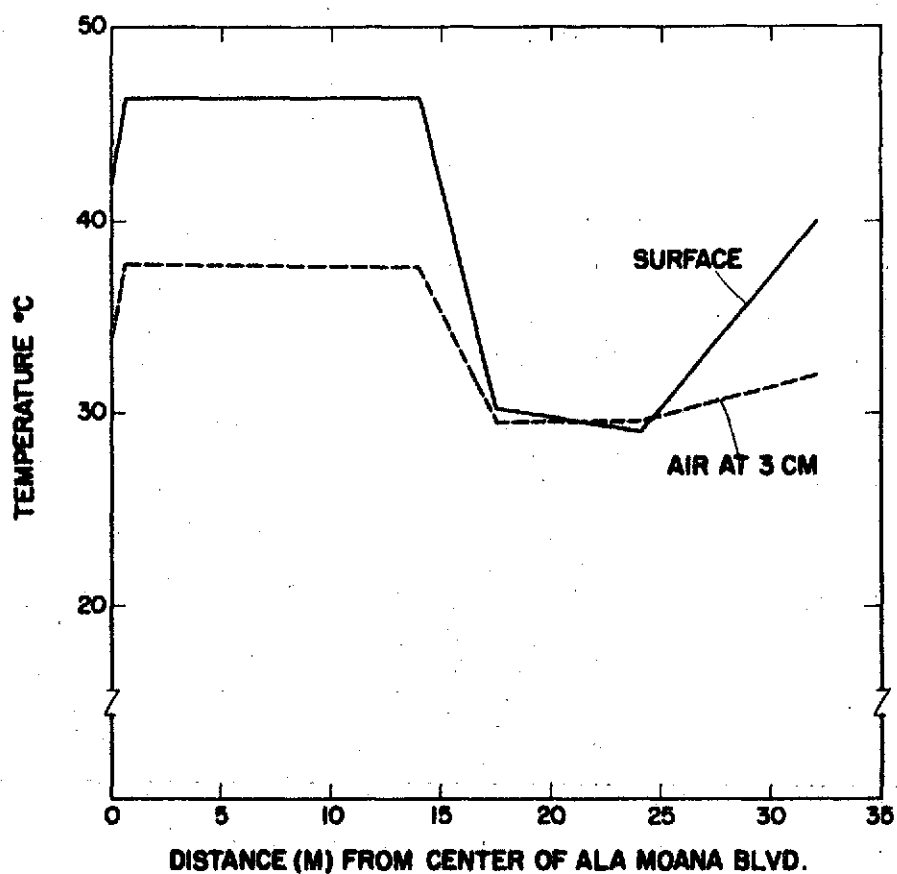
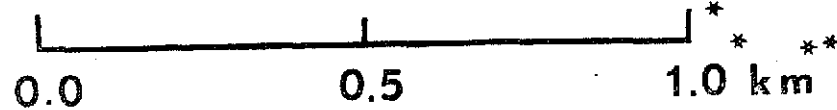


Fig. 3. Temperatures at ground surface and 3 cm above ground along a portion of a transect line extending from the center of Ala Moana Blvd. at Piikoi St. across Ala Moana Park, August 4, 1972. The 24 hour mean annual temperature for Honolulu is 23.9° centigrade.

Fig. 4. Sampling Stations in the Ala Wai Canal and Yacht Harbor. Station codes are TWC, midchannel opposite Texaco Fuel Dock; TD, at the Texaco Fuel Dock; HYC, midchannel opposite the Hawaii Yacht Club; SDH, midchannel opposite the dock with a large sign reading "Skindivers Hawaii"; AMB, midchannel by Ala Moana Bridge; KPOI, midchannel opposite the transmitting tower of radio station KPOI; KB, midchannel by the Kalakaua Bridge; AS, the entrance of Apukehau Stream; MB, midchannel by the McCully Bridge; KUA, midchannel by Kuamoo Street; MPD, the confluence of the Manoa-Palolo Drainage Canal and the Ala Wai Canal; MPDD, a dock on the Manoa-Palolo Canal about 100 m upstream of the Ala Wai; KAN, midchannel opposite Kanekapolei Street; PAO, midchannel opposite Paoakalani Street; END, the extreme landward end of the Canal near Kapahulu Blvd.



The levels of mercury at various sampling stations in the Ala Wai are presented in Table 4. Figure 5 shows these levels as a function of the distance upstream from a point in the center of the boat channel opposite the Texaco fuel dock. There is a significant linear regression of the amounts of mercury in Ala Wai sediments (\log_{10} converted) on the distance upstream from that point, indicating a source of mercury either in the harbor or seaward of the harbor. The few mercury values recorded seaward of the harbor and off Waikiki beach (Table 5) are low in comparison to harbor values.

On March 6, the water in the harbor contained $0.6 \mu\text{g liter}^{-1}$ while the level in water at the juncture of the Manoa-Palolo Drainage Canal and Ala Wai contained $0.3 \mu\text{g liter}^{-1}$. On all other sampling dates the mercury contents of canal and harbor waters never exceeded the limit of detection, $0.1 \mu\text{g liter}^{-1}$. This suggests that the source of some of the mercury in the Ala Wai is intermittent. Though it has not been possible to identify the source, there are several industries in the harbor area as well as a large hospital which might be responsible. Mercury-containing anti-fouling paints are probably a continuous source of the metal in the harbor.

Though the Ala Wai and perhaps the Ala Moana data appear to represent industrial mercury contamination, an examination of the mercury contents of various materials from less populated areas does not reveal the great differences that would be expected if industrial

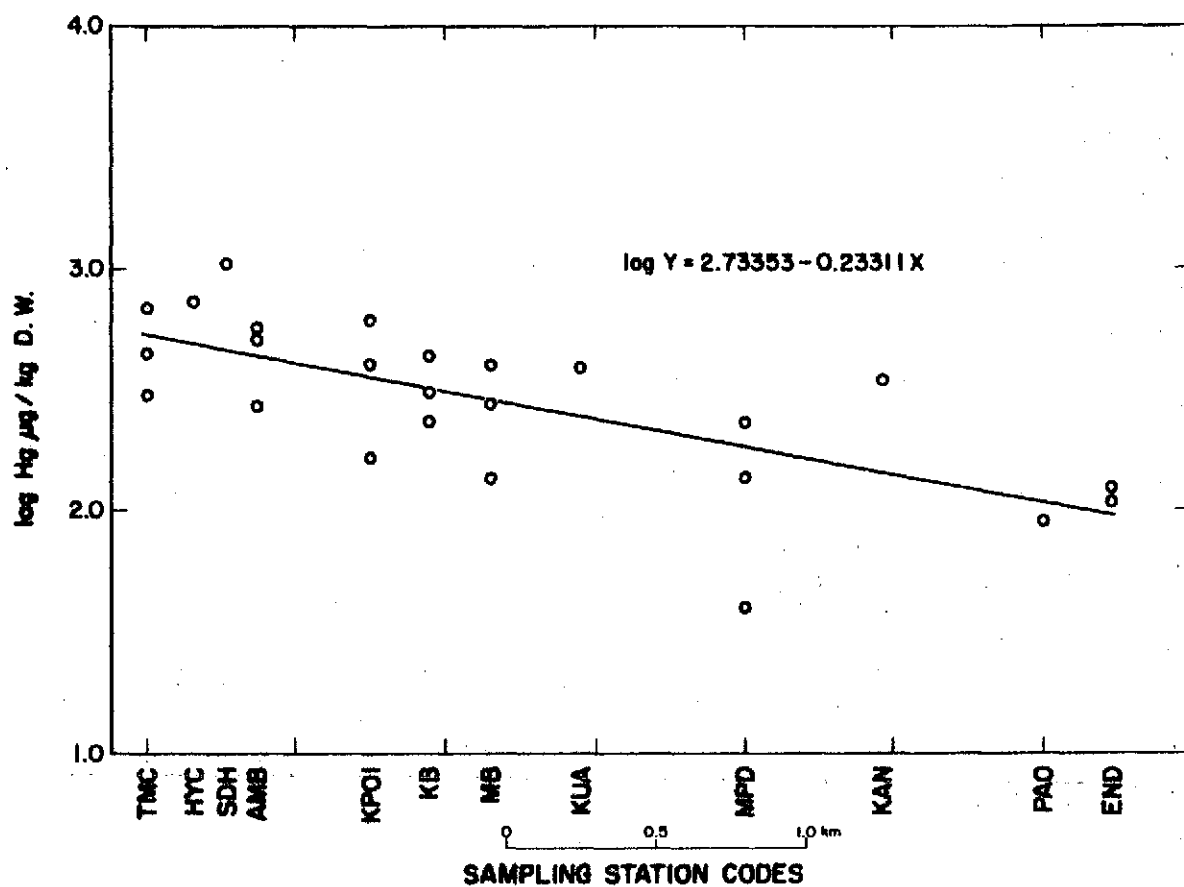


Fig. 5. Mercury in the Ala Wai Canal and Yacht Harbor sediments as a function of distance from Texaco Fuel Dock.

Table 5

Mercury in the Hawaiian Environment

Air

Collection Site and Date	Mercury Content (μg per cubic meter)
Manoa Campus, University of Hawaii, Hon. April 18, 1971	0.04 ± 0.02
Ala Moana Blvd. at Piikoi Street, Hon. August 4, 1972	0.14 ± 0.10
August 10, 1972	n.d.
Sulfur Banks, HVNP. April 10, 1971	23.3 ± 5.4
May 8, 1971	21.4 ± 8.5
January 9, 1972	2.2 ± 1.0
April 16, 1972	33.5 ± 7.4
Halemaumau Caldera, HVNP August 18, 1971	40.5
January 9, 1972	0.73

Table 5 (continued)

Mercury in the Hawaiian Environment

Water

Collection Site and Date	Mercury Content ($\mu\text{g liter}^{-1}$)
Pacific Ocean off Waikiki, Hon.	
January 15, 1971	0.1
Keehi Lagoon, Hon.	
January 6, 1971	0.2
Kapalama Canal, Hon.	
January 5, 1971	0.2
Ala Wai Canal and Yacht Harbor, Hon.	
January 7, 1971.	0.1
July 14, 1971	0.1
March 6, 1972	0.3-0.6
^a Sewage Water, Sand Island Outfall, Hon.	
December 15, 1970	10.0
^b Kaukonahua Stream at Waialua, Oahu	
October 7, 1970	0.1
^b Waikele Stream at Waipahu, Oahu	
October 7, 1970	0.7
^b Nuuanu Stream near Honolulu	
October 7, 1970	0.6
^b Manoa-Palolo Drainage Canal, Hon.	
October 7, 1970	0.1

Table 5 (continued)

Mercury in the Hawaiian Environment

Water (continued)		Mercury Content ($\mu\text{g liter}^{-1}$)
Collection Site and Date		
<i>b</i> Kawainui Drainage Canal, Kailua, Oahu		
October 7, 1970		0.1
<i>b</i> Wailuku River at Piihonua, Maui		
October 13, 1970		0.1
<i>b</i> Honolii Stream near Papaikou, Hawaii		
October 13, 1970		1.2
<i>b</i> Kalihi Stream at Nimitz Bridge, Hon.		
October 7, 1970		1.0
Fumarole Condensates, Sulfur Banks, HVNP		
April 18, 1971		20-40
Rainwater, 7 sites on Hawaii		
January 21-28, 1972		0.17 ± 0.05
Rainwater, Lihue, Kauai		
January 21-28, 1972		0.15

Table 5 (continued)

Mercury in the Hawaiian Environment

Soil, Sediments and Rocks

Collection Site and Date	Mercury Content ($\mu\text{g kg}^{-1}$)
Ala Moana Park Soils, Hon.	
August 10, 1972	32-460 DW
Ala Wai Canal and Yacht Harbor, Hon.	
March 6, 1972	90-1340 DW
Sandy Bottom 5-65 m. off Waikiki, Hon.	
February, 1972	32-63 DW
Assorted Soils, Hawaii	
January 28, 1972	17-302 DW
Keehi Lagoon, Hon.	
January 6, 1971	195 FW
Kapalama Canal, Hon.	
January 6, 1972	80-210 FW
December, 1970	350 FW
Lava, Halemaumau Caldera, Hawaii	
August, 1971	700-750 FW
Sulfur Crust, Sulfur Banks, Hawaii	
April, 1972	1100 FW

Table 5 (continued)

Mercury in the Hawaiian Environment

Biological Materials

Collection Site and Date	Mercury Content ($\mu\text{g kg}^{-1}$)
Grasses	
Ala Moana Park, Hon., Oahu, August 4, 1972	60-240 DW
Grasses	
Various Sites, Hawaii, January 28, 1972	26-188 FW
Assorted Higher Plants	
Manoa Valley, Hon.	13-18
Assorted Higher Plants	
Sulfur Banks, HVNP, August 18, 1971	17-158
<i>Lyngbea</i> sp.	
Waikiki, Hon., February, 1972	90-163 DW
Noddy Tern, <i>Anous stolidus</i> , Tailfeathers	
Windward Oahu, June, 1971	510 \pm 200
White-capped Noddy Tern	
<i>Anous Melonogenys minutus</i> , Tailfeathers	
Windward Oahu, June, 1971	270 FW
Sooty tern, <i>Sterna fuscata</i> , Tailfeathers	
Windward Oahu, June, 1971	720 FW
^c Pacific Blue Marlin, <i>Makaira ampla</i>	
Off Hawaii, August, 1971	350-14,000 FW
^c Yellow Fin Tuna, <i>Neothunnus macropterus</i>	
Various Pacific waters	220-1,320 FW
Assorted small fish	
Oahu, March, 1971	49 \pm 57
Beef Kidney	
Hawaii, December, 1970	150

Table 5 (continued)

Abbreviations:	(Hon.)	Honolulu, Oahu
	HVND	Hawaii Volcanoes National Park, Hawaii
	(DW)	Dry weight
	(FW)	Fresh weight

^a data from Oahu Water Quality Program

^b data from Durum, Hem and Heidel (1971)

^c data from Rivers, *et al.* (1972)

contamination were a major source. In fact, in the Hawaiian Islands as a whole, industrial mercury contamination appears to be insignificant.

This is not the case with lead. For example, heavily contaminated roadside grasses in Honolulu may contain 100 times the lead found in grasses from remote areas on other islands. Roadside soils may contain 50 to 100 times the lead found in soil 100 m downwind of the same road. Such a striking concentration gradient with respect to source is not seen with mercury. Mercury levels comparable or greater than those found in Ala Moana Park soils have been observed in relatively remote areas of the island of Hawaii (Table 5). It is suspected that volcanic activity is the source of the majority of mercury in the Hawaiian environment.

Several observations support this hypothesis. First, fumaroles in the Hawaiian Volcanoes National Park are producing significant quantities of mercury (Eshleman *et al.* 1971) as a gas (Table 5). Though the comparison between concentrated fumarole gases at the Sulfur Banks and the clean air of the Manoa Valley of Oahu some 320 km NW is not in itself that valid, subsequent observations have strengthened the suspicion that the major part of the mercury in Hawaiian air originates from active vulcanism. On August 15, 1971, during a peak of significant volcanic activity, an integrated air sample taken from a moving car 55 to 40 km NW of the Sulfur Banks site showed a mercury content of $1.8 \mu\text{g m}^{-3}$. The criticism that

this may represent contamination by vehicle exhaust is answered by additional data. On August 4, 1972, also a period of high volcanic activity, Oahu air samples from the intersection of Ala Moana Blvd. and Piikoi Street, a previously mentioned region of high traffic density, showed a mercury content of $0.14 \mu\text{g m}^{-3}$. The prevailing winds at this time were SW or "Kona" coming from the direction of the island of Hawaii. A further series of air samples from this same site taken some six days later during a period of NE tradewind activity showed no detectable mercury (less than $0.03 \mu\text{g m}^{-3}$) despite the fact that traffic volume was unchanged.

A collection of higher plants from the Sulfur Banks site showed a mean mercury content (fresh weight bases) of $53 \pm 45 (\mu\text{g kg}^{-1}$ per billion) whereas a collection from the Manoa Valley showed 21 ± 11 . The Manoa Valley is only 5 km from the industrial areas of Honolulu.

The mercury content of various lavas and sulfur deposits at the Hawaii Volcanoes National Park varies widely (Table 5), but includes several high values. It is noteworthy that the highest value for lava, $700\text{--}750 \mu\text{g kg}^{-1}$ was obtained from a sample that was collected within 24 hours of extrusion. A more extensive treatment of geothermal sources and distribution of mercury is presently in preparation by Siegel and others.

Rainwater from Hawaii was analyzed in an attempt to establish correlations between its mercury content and proximity to the suspected volcanic source. Figure 6 shows the mercury content of rainfall

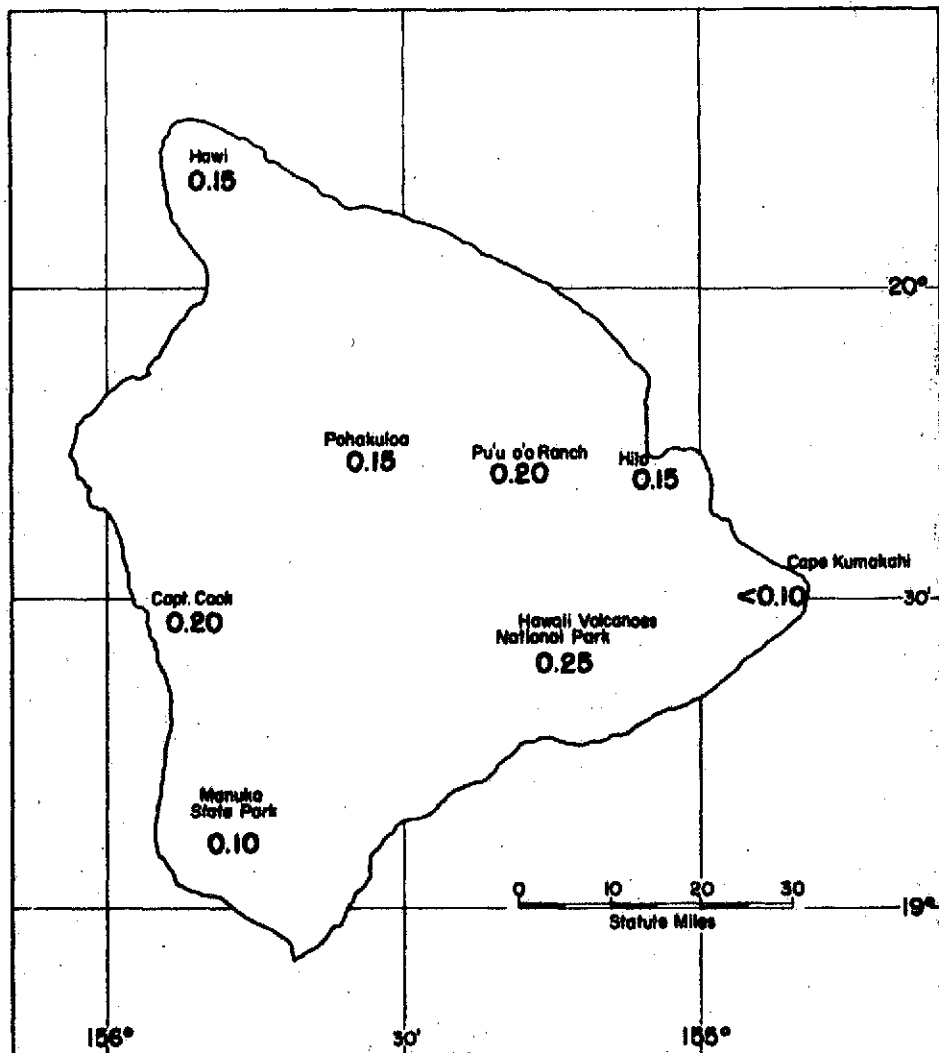


Fig. 6. Mercury content of rainfall in ppb at selected sites on the island of Hawaii for the week January 21-28, 1972. All sites are United States Weather rain gauges. Gauge locations are (clockwise from top) Hawi, Pu'u o'o Ranch, Hilo Airport, The Orr Residence at Cape Kamukahi, Headquarters Building at Hawaii Volcanoes National Park, Manuka State Park, Greenwell Residence at Captain Cook and Pohakuloa State Park.

from eight sites on the island. The mean mercury content of seven samples in which detectable mercury was present is $0.17 \pm 0.05 \mu\text{g liter}^{-1}$. This is remarkably good agreement with Stock and Cucuel's (1934) measurements of $0.20 \mu\text{g liter}^{-1}$ for rainfall collected in Germany during the 1930's. The highest level, $0.25 \mu\text{g liter}^{-1}$ was found in the sample from the Hawaiian Volcanoes National Park and the lowest from Cape Kamukahi. The high value may reflect mercury discharges from nearby volcanic activity, but it does not differ significantly from the mean. The prevailing winds at Cape Kamukahi are NE trades off the ocean. The low value at this site may thus be explained by either its location upwind of the volcanic source or the observation that air above open seas is generally lower in mercury content than that above landmasses. The observation at Cape Kamukahi is further complicated by the observation that rainfall at Hilo contained 0.15 ppb despite the fact that circulation at this site is similar. The Hilo collection point was at an airport. Perhaps the mercury in this sample represents contamination by aircraft exhaust emissions. In support of this is the observation that rainfall at the Lihue, Kauai, airport during the same 7 day period contained 0.15 ppb.

At present, the most that can be said for the rainfall data is that they are inconclusive. A more extensive study would take into account the myriad of variables involved, but this is beyond the scope of this dissertation.

Conclusions

It has been difficult to put the whole problem of environmental mercury contamination into proper perspective for a variety of reasons. First, the metal itself is remarkable for having an appreciable vapor pressure at relatively low temperatures. Mercury is a small but always present component of the earth's atmosphere. Mercury does not require human activities for its liberation from ore deposits. Second, the bulk of the literature on mercury contamination during the last decade has dealt with some obvious and frequently terrible instances of industrial contamination. This has caused the general public and some members of the scientific community to approach the problem of mercury distribution as a pollution problem. An example of this is the worldwide concern over mercury levels in fish. In 1970, Fimreite (Montague and Montague 1971) clearly showed that mercury wastes from a plastics factory had contaminated large portions of waterway and elevated the mercury levels of fish in the same waterway. Shortly after this, McDuffie (Montague and Montague 1971) showed that tuna also had high levels of mercury in their muscle tissue. Subsequent reports confirmed the high mercury levels in tuna and showed that marlin and swordfish had even higher levels. This and the fact that the United States Food and Drug Administration standards required that all foods containing more than $500 \mu\text{g kg}^{-1}$ mercury (fresh weight) must be removed from sale, seriously depressed portions

of the fishing industry and created the impression that these fish had been polluted.

Recent reports have indicated that pollution may not be involved (Hammond 1971). Tuna and swordfish that have been preserved for as long as 93 years showed mercury contents which also exceeded the FDA standard and did not differ significantly from contemporary values (Miller *et al.* 1972). Further, indications exist in the literature that fish are unique among biota in having high levels of mercury. Stock and Cucuel (1934) in a survey of mercury in the environment which has not been seriously challenged in 38 years, stated: "the mercury content of fresh and saltwater fish is strikingly high." It is unfortunate that Stock and Cucuel did not analyze any of the large ocean-going food fishes because the values they present for smaller fish ($28-180 \mu\text{g kg}^{-1}$) are in good agreement with contemporary values (Table 5).

Perhaps the strongest evidence that mercury in the Hawaiian environment originates from a volcanic source is temporal. The Hawaiian chain is entirely volcanic in origin. These volcanic processes have continued for 5-10 million years. While mercury levels in the environment are not characteristic of gross contamination, they are sufficiently high to warrant speculation as to source. It is possible that the majority of the mercury liberated with the volcanic birth of these islands has entered global circulation. High mean temperatures and prevalent tradewinds of Hawaii suggest a mechanism by

which this mercury could be spread. Perhaps some of the mercury in fish had its origin as a volcanic discharge. Volcanic activity may be a greater source of mercury than has been previously suspected.

Some of the principle findings in support of the conclusion that mercury enters the Hawaiian environment as a natural product of vulcanism are listed below:

1. No major industrial source of mercury could be identified in Hawaii. In one study, mercury levels in roadside soils and vegetation appeared to be higher in proximity to motor vehicle traffic, though the distribution pattern was different than that for lead. Motor vehicle traffic is probably not a major source of mercury since soils and plants from areas far-removed from heavy concentrations of traffic were frequently found to contain amounts of mercury in excess of the roadside value. There was a significant relationship between the mercury contents of sediments in the Ala Wai Canal and Yacht Harbor and the proximity of the sediment samples to the Harbor area. This suggests that some activity associated with boating is a source of this mercury. Mercury-containing anti-fouling paints are the most probable source.

2. Fumarole gases in volcanic areas on the island of Hawaii were found to contain $2.2\text{--}40.5 \mu\text{g Hg/m}^3$. Atmospheric transport from geothermal areas on Hawaii as well as the general volcanic history of the island chain appear to offer the best explanation for the presence of mercury in various materials in the Hawaiian Environment.

Mercury issuing from a volcanic source is impossible to control. Indeed, it may not be necessary to consider controls unless a hazard to the public or environmental health is suspected. The health aspects of volcanic mercury constitute a logical next phase of mercury research. Such research has great importance in view of the observation that:

The difference between tolerable natural background levels [of mercury] in the environment and levels harmful to man and animals is very small (Hammond 1971).

The presence of a natural emission source — active vulcanism — may provide clues as to just how much of certain substances may be natural in undisturbed environments.

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